

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SANYO ELECTRIC CO LTD

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(72)Inventor : JINNO MARUO  
UEHARA MAYUMI  
SAKURAI ATSUSHI  
NISHIO KOJI  
SAITO TOSHIHIKO

## (54) NONAQUEOUS ELECTROLYTE BATTERY

(57)Abstract:

PURPOSE: To enhance storage characteristics.

CONSTITUTION: 1-20vol.% specific additive is added to a nonaqueous electrolyte prepared by dissolving lithium trifluoromethane sulfonate or lithium hexafluorophosphate in a solvent containing at least one high dielectric constant solvent selected from the group comprising ethylene carbonate, propylene carbonate, and butylene carbonate. The additive reacts with lithium or the like to form a film on the surface of a negative electrode, the film makes the reaction of the negative electrode with the nonaqueous electrolyte difficult to occur, and thereby self discharge hardly occur even when a battery is stored for a long time.

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**CLAIMS**

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[Claim(s)]

[Claim 1] Positive electrode. The negative electrode which makes a lithium an active material. Nonaqueous electrolyte which comes to melt a trifluoromethane sulfonic-acid lithium or a hexafluoro phosphoric-acid lithium to the solvent containing at least a kind of high dielectric constant solvent chosen from the group which consists of ethylene carbonate, propylene carbonate, and butylene carbonate. Separator. It is the nonaqueous electrolyte cell equipped with the above. the aforementioned nonaqueous electrolyte A triethylamine, N butylamine, an aniline, a trimethyl hydroxylamine, 1-dimethylamino-2-methoxyethane, An acetonitrile, acrylonitrile, 3-methoxy propionitrile, Benzonitrile, nitromethane, nitroethane, N, and N-dimethylacetamide, N,N-dimethylformamide, a formamide, a N-methyl-2-pyrrolidone, N and N'-dimethyl imidazolidinone, iso KISAZORU, 3, 5-dimethyl iso KISAZORU, 3-methyl-2-oxazolidone, 1 and 2, 3-OKISA diazole, N-methyl morpholine, a dimethyl sulfide, an ethyl methyl sulfide, 2-methylthiophene, 1-butane thiol, a benzene thiol, dimethyl sulfate, Diethyl sulfate, a dimethyl ape fight, a diethyl ape fight, A butadiene sulfone, 3-methyl SURUHOREN, 1, 4-thioxan, FENO key search in, 1, 4-thia gin, a thio morpholine, a pyridine, It is characterized by doing 1-20 volume % content of at least one sort of additives chosen from the group which consists of 1, 3-dimethyl-2-imidazolidinone, dimethyl sulfoxide, a dimethyl sulfone, methylethyl sulfonate, and a dimethyl SURUFI night.

[Claim 2] The nonaqueous electrolyte cell according to claim 1 by which the aforementioned nonaqueous electrolyte contains further 1 and 2-dimethoxyethane.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to improvement of nonaqueous electrolyte aiming at improving the preservation property of a nonaqueous electrolyte cell in detail with respect to a nonaqueous electrolyte cell.

[0002]

[Description of the Prior Art] When a nonaqueous electrolyte cell equipped with the negative electrode which makes a lithium an active material selects the active material of a positive electrode suitably in recent years, it is observed from high-capacity-izing being possible.

[0003] By the way, as a negative electrode which makes a lithium an active material, the metal lithium, the lithium alloy, the carbon material, etc. are proposed.

[0004] However, generally such negative-electrode material tends to react with nonaqueous electrolyte during preservation, and when saved for a long period of time, there is a problem that service capacity decreases remarkably by self-discharge in the nonaqueous electrolyte cell which makes a lithium the active material of a negative electrode for this reason.

[0005] The place which this invention is made to solve this problem and is made into the purpose is by suppressing the self-discharge resulting from the reaction of a negative electrode and nonaqueous electrolyte to offer the nonaqueous electrolyte cell which has the outstanding preservation property.

[0006]

[Means for Solving the Problem] The nonaqueous electrolyte cell (this invention cell) concerning this invention for attaining the above-mentioned purpose A positive electrode, the negative electrode which makes a lithium an active material, and ethylene carbonate, The nonaqueous electrolyte which comes to melt a trifluoromethane sulfonic-acid lithium or a hexafluoro phosphoric-acid lithium at least to a kind of high dielectric constant solvent chosen from the group which consists of propylene carbonate and butylene carbonate, It is a nonaqueous electrolyte cell equipped with separator. the aforementioned nonaqueous electrolyte A triethylamine, n butylamine, an aniline, a trimethyl hydroxylamine, 1-dimethylamino-2-methoxyethane, an acetonitrile, acrylonitrile, 3-methoxy propionitrile, a benzonitrile, a nitromethane, a nitroethane, N and N-dimethylacetamide, N,N-dimethylformamide, a formamide, N-methyl-2-pyrrolidone, N, and N'-dimethyl imidazolidinone, Iso KISAZORU, 3, 5-dimethyl iso KISAZORU, 3-methyl-2-oxazolidone, 1, 2, 3-OKISA diazole, N-methyl morpholine, a dimethyl sulfide, An ethyl methyl sulfide, 2-methylthiophene, 1-butane thiol, A benzene thiol, dimethyl sulfate, diethyl sulfate, A dimethyl ape fight, a diethyl ape fight, a butadiene sulfone, 3-methyl SURUHOREN, 1, 4-thioxan, FENO key search in, 1, 4-thia gin, 1-20 volume % content of at least one sort of additives chosen from the group which consists of a thio morpholine, a pyridine, 1, 3-dimethyl-2-imidazolidinone, dimethyl sulfoxide, a dimethyl sulfone, methylethyl sulfonate, and a dimethyl SURUFI night is done.

[0007] The nonaqueous electrolyte of this invention cell does 1-20 volume % content of a specific additive. If additive content separates from this range, a preservation property will stop being able to improve easily.

[0008] A preservation property is further improvable if the mixed solvent which added 1 and 2-dimethoxyethane to the above-mentioned quantity dielectric constant solvent is used as a solvent of nonaqueous electrolyte. The ranges of the suitable content ratio of the high dielectric constant solvent in that case and 1 and 2-dimethoxyethane are 3:7-7:3 in a volume ratio.

[0009] As an example of the negative electrode which makes a lithium an active material, what used lithium alloys (a lithium aluminium alloy, a lithium and a lead alloy, a lithium, a tin alloy, etc.), metallic oxides (LiNb 2O5 etc.), or carbon materials (a graphite, corks, organic substance baking object, etc.) for negative-electrode material is mentioned.

[0010] this invention has the feature in the point which used what carries out specified quantity content of the specific additive as nonaqueous electrolyte to improve the preservation property of a nonaqueous electrolyte cell equipped with a specific negative electrode and specific nonaqueous electrolyte. Therefore, about other members which constitute cells, such as a positive electrode and separator, the various things currently used [ which are used and are former-proposed ] as an object for nonaqueous electrolyte cells can be used. Moreover, this invention is applicable to both a primary cell and a rechargeable battery.

[0011]

[Function] The specific additive which nonaqueous electrolyte was made to contain, and the lithium in the solvent and solute in nonaqueous electrolyte, and a negative electrode react, and a coat is formed in a negative-electrode front face. Since the reaction of a negative electrode and nonaqueous electrolyte stops

being able to happen easily, self-discharge is suppressed by this coat. Consequently, even when saved for a long period of time, service capacity stops being able to decrease easily (improvement in a preservation property). In addition, since electronic conductivity of a coat is good, the electrode reaction in a negative electrode is not checked by forming a coat in a negative electrode.

[0012]

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0013] [Production of a positive electrode] Manganese dioxide as an active material (manganese dioxide heat-treated by 375 degreeC), the acetylene black as an electric conduction agent, and the polyvinylidene fluoride as a binder — the weight ratio 80:10:10 — mixing — a positive electrode — a mixture — preparing — this positive electrode — after made the N-methyl-2-pyrrolidone distribute a mixture, having prepared the slurry, having applied this slurry on the aluminum foil, rolling it out and piercing with a diameter of 20mm in the shape of a disk, it heat-treated by 150 degreeC for 2 hours, and the positive electrode was produced

[0014] [Production of a negative electrode] The metal lithium rolled plate was pierced with a diameter of 20mm in the shape of a disk, and the negative electrode was produced.

[0015] [Manufacture of nonaqueous electrolyte] To the solvent which shows composition in Table 1 - 6, a trifluoromethane sulfonic-acid lithium ( $\text{LiCF}_3\text{SO}_3$ ) or one mol ( $\text{LiPF}_6$ ) /of hexafluoro phosphoric-acid lithiums was melted l., and nonaqueous electrolyte was prepared to it.

[0016]

[Table 1]

溶媒組成比 (体積比)	溶質	自己放電率 (%)
BC:DME = 50:50 (比較電池)	$\text{LiCF}_3\text{SO}_3$	14
BC:DME:トリエチルアミン = 47.5:47.5:5 (本発明電池 X)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:n-ブチルアミン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:7-ノルボルネン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:トリメチルヒドロキシメチル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:1-トリメチルアミン-2-メチルプロピル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:7-ノルボルネン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:7-ノルボルネン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:3-メチルプロピル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ペンタメチル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:ニトロメチル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ニトロメチル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:N,N-ジメチルセチル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:N,N-ジメチルセチル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:セチル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:N-メチル-2-ピロリドン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:N,N'-ジメチルイミダゾリル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:イソキソル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:3,5-ジメチルイソキソル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:3-メチル-2-メチルプロピル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:1,2,3-トリメチルプロピル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:N-メチルセチル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4

[0017]

[Table 2]

溶媒組成比 (体積比)	溶質	自己放電率 (%)
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:トリメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:2-メチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:1-ブチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ペンタメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:3-メチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:1,4-ジオキソラン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:7-メチルジオキソラン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:1,4-ジオキソラン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ジオキソラン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ジオキソラン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4
BC:DME:ジオキソラン = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:1,3-ジメチル-2-イミダゾリル = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	3
BC:DME:トリメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	5
BC:DME:ジメチルホルムアミド = 47.5:47.5:5 (本発明電池)	$\text{LiCF}_3\text{SO}_3$	4

[0018]

[Table 3]

溶媒組成比 (体積比)		溶質	自己放電率 (%)
EC	= 100	LiCF <sub>3</sub> SO <sub>3</sub> LiCF <sub>3</sub> SO <sub>3</sub>	1 8 5
EC:トリエチレンジミン	= 95:5 (比較電池) (本発明電池 Y)		

[0019]

[Table 4]

溶媒組成比 (体積比)		溶質	自己放電率 (%)
EC:DME	= 50:50 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 9
EC:DME:トリエチレンジミン	= 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
PC:DME	= 50:50 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 6
PC:DME:トリエチレンジミン	= 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
BC:DME	= 50:50 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 4
BC:DME:トリエチレンジミン	= 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME	= 50:50 (比較電池)	LiPF <sub>6</sub>	2 1
EC:DME:トリエチレンジミン	= 47.5:47.5:5 (本発明電池)	LiPF <sub>6</sub>	5
PC:DME	= 50:50 (比較電池)	LiPF <sub>6</sub>	1 8
PC:DME:トリエチレンジミン	= 47.5:47.5:5 (本発明電池)	LiPF <sub>6</sub>	5
BC:DME	= 50:50 (比較電池)	LiPF <sub>6</sub>	1 6
BC:DME:トリエチレンジミン	= 47.5:47.5:5 (本発明電池)	LiPF <sub>6</sub>	4

[0020]

[Table 5]

溶媒組成比 (体積比)		溶質	自己放電率 (%)
EC:PC:DME	= 1:1:1 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 4
EC:PC:DME:トリエチレンジミン	= 32:32:32:4 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:BC:DME	= 1:1:1 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 3
EC:BC:DME:トリエチレンジミン	= 32:32:32:4 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
PC:BC:DME	= 1:1:1 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 3
PC:BC:DME:トリエチレンジミン	= 32:32:32:4 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4

[0021]

[Table 6]

添加剤組成比 (体積比)		溶質	自己放電率 (%)
BC:DME:トリエチレンジミン	= 49.95:49.95:0.1 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 3
BC:DME:トリエチレンジミン	= 49.75:49.75:0.5 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 2
BC:DME:トリエチレンジミン	= 49.5:49.5:1 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
BC:DME:トリエチレンジミン	= 45:45:10 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
BC:DME:トリエチレンジミン	= 40:40:20 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
BC:DME:トリエチレンジミン	= 35:35:30 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 8

[0022] [Assembly of a cell] The nonaqueous electrolyte cell of various flat types was assembled using the above positive electrode, negative electrode, and nonaqueous electrolyte (cell size : 2.5mm in the diameter of 20.0mm, thickness). In addition, as separator, the fine porous membrane made from polypropylene was used, and previous nonaqueous electrolyte was infiltrated into this.

[0023] [Rate of self-discharge of each cell] The service capacity C2 in 25 degreeC after saving for two months by the service capacity C1 in 25 degreeC immediately after the cell assembly of each cell and 80 degreeC was calculated, and the rate of self-discharge after preservation of each cell was computed by the lower formula. Altogether, by constant resistance of 1kohm, service capacity C1 and C2 discharges, and is calculated. A result is shown in previous Table 1 - 6. in addition, front Naka and EC — ethylene carbonate — PC — propylene carbonate — BC — butylene carbonate — moreover, DME expresses 1 and 2-dimethoxyethane, respectively

[0024]

Rate (%) of self-discharge =  $(1 - C2/C1) \times 100$ . [0025] As shown in Table 1 - 5, this invention cell which used the nonaqueous electrolyte (each additive content is 5 volume %) containing a specific additive has a low rate of self-discharge compared with the comparison cell by which the solvent and solute which do not contain an additive used the same nonaqueous electrolyte. This shows that the nonaqueous electrolyte cell which was excellent in the preservation property by making nonaqueous electrolyte contain a specific additive is obtained.

[0026] Moreover, since the rate of self-discharge is low compared with this invention cell Y in Table 3, when this invention cell X in Table 1 uses the mixed solvent of a high-rate-discharge solvent and 1 and 2-dimethoxyethane show that the nonaqueous electrolyte cell which was further excellent in the preservation property is obtained.

[0027] Furthermore, if additive content separates from this range to a thing with the very as low rate of self-discharge as 5% when additive content is made into one to 20 volume % as shown in Table 6, the rate of

self-discharge will become high. This shows that it is necessary to regulate the additive content of nonaqueous electrolyte in the range of 1 – 20 volume %.

[0028]

[Effect of the Invention] An additive reacts with a lithium etc., a coat is formed on the surface of a negative electrode, and since this coat makes it hard to happen the reaction of a negative electrode and nonaqueous electrolyte, even when saved for a long period of time, self-discharge cannot happen easily. For this reason, this invention cell is excellent in a preservation property.

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**TECHNICAL FIELD**

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] An additive reacts with a lithium etc., a coat is formed on the surface of a negative electrode, and since this coat makes it hard to happen the reaction of a negative electrode and nonaqueous electrolyte, even when saved for a long period of time, self-discharge cannot happen easily. For this reason, this invention cell is excellent in a preservation property.

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TECHNICAL PROBLEM

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[0004] However, generally such negative-electrode material tends to react with nonaqueous electrolyte during preservation, and when saved for a long period of time, there is a problem that service capacity decreases remarkably by self-discharge in the nonaqueous electrolyte cell which makes a lithium the active material of a negative electrode for this reason.

[0005] The place which this invention is made to solve this problem and is made into the purpose is by suppressing the self-discharge resulting from the reaction of a negative electrode and nonaqueous electrolyte to offer the nonaqueous electrolyte cell which has the outstanding preservation property.

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## MEANS

[Means for Solving the Problem] The nonaqueous electrolyte cell (this invention cell) concerning this invention for attaining the above-mentioned purpose A positive electrode, the negative electrode which makes a lithium an active material, and ethylene carbonate, The nonaqueous electrolyte which comes to melt a trifluoromethane sulfonic-acid lithium or a hexafluoro phosphoric-acid lithium at least to a kind of high dielectric constant solvent chosen from the group which consists of propylene carbonate and butylene carbonate, It is a nonaqueous electrolyte cell equipped with separator. the aforementioned nonaqueous electrolyte A triethylamine, n butylamine, an aniline, a trimethyl hydroxylamine, 1-dimethylamino-2-methoxyethane, an acetonitrile, acrylonitrile, 3-methoxy propionitrile, a benzonitrile, a nitromethane, a nitroethane, N and N-dimethylacetamide, N,N-dimethylformamide, a formamide, N-methyl-2-pyrrolidone, N, and N'-dimethyl imidazolidinone, Iso KISAZORU, 3, 5-dimethyl iso KISAZORU, 3-methyl-2-oxazolidone, 1, 2, 3-OKISA diazole, N-methyl morpholine, a dimethyl sulfide, An ethyl methyl sulfide, 2-methylthiophene, 1-butane thiol, A benzene thiol, dimethyl sulfate, diethyl sulfate, A dimethyl ape fight, a diethyl ape fight, a butadiene sulfone, 3-methyl SURUHOREN, 1, 4-thioxan, FENO key search in, 1, 4-thia gin, 1-20 volume % content of at least one sort of additives chosen from the group which consists of a thio morpholine, a pyridine, 1, 3-dimethyl-2-imidazolidinone, dimethyl sulfoxide, a dimethyl sulfone, methylethyl sulfonate, and a dimethyl SURUFI night is done.

[0007] The nonaqueous electrolyte of this invention cell does 1-20 volume % content of a specific additive. If additive content separates from this range, a preservation property will stop being able to improve easily.

[0008] A preservation property is further improvable if the mixed solvent which added 1 and 2-dimethoxyethane to the above-mentioned quantity dielectric constant solvent is used as a solvent of nonaqueous electrolyte. The ranges of the suitable content ratio of the high dielectric constant solvent in that case and 1 and 2-dimethoxyethane are 3:7-7:3 in a volume ratio.

[0009] As an example of the negative electrode which makes a lithium an active material, what used lithium alloys (a lithium aluminium alloy, a lithium and a lead alloy, a lithium, a tin alloy, etc.), metallic oxides (LiNb 2O5 etc.), or carbon materials (a graphite, corks, organic substance baking object, etc.) for negative-electrode material is mentioned.

[0010] this invention has the feature in the point which used what carries out specified quantity content of the specific additive as nonaqueous electrolyte to improve the preservation property of a nonaqueous electrolyte cell equipped with a specific negative electrode and specific nonaqueous electrolyte. Therefore, about other members which constitute cells, such as a positive electrode and separator, the various things currently used [ which are used and are former-proposed ] as an object for nonaqueous electrolyte cells can be used. Moreover, this invention is applicable to both a primary cell and a rechargeable battery.

[Translation done.]

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**OPERATION**

[Function] The specific additive which nonaqueous electrolyte was made to contain, and the lithium in the solvent and solute in nonaqueous electrolyte, and a negative electrode react, and a coat is formed in a negative-electrode front face. Since the reaction of a negative electrode and nonaqueous electrolyte stops being able to happen easily, self-discharge is suppressed by this coat. Consequently, even when saved for a long period of time, service capacity stops being able to decrease easily (improvement in a preservation property). In addition, since electronic conductivity of a coat is good, the electrode reaction in a negative electrode is not checked by forming a coat in a negative electrode.

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[Translation done.]

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## EXAMPLE

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0013] [Production of a positive electrode] Manganese dioxide as an active material (manganese dioxide heat-treated by 375 degreeC), the acetylene black as an electric conduction agent, and the polyvinylidene fluoride as a binder — the weight ratio 80:10:10 — mixing — a positive electrode — a mixture — preparing — this positive electrode — after made the N-methyl-2-pyrrolidone distribute a mixture, having prepared the slurry, having applied this slurry on the aluminum foil, rolling it out and piercing with a diameter of 20mm in the shape of a disk, it heat-treated by 150 degreeC for 2 hours, and the positive electrode was produced.

[0014] [Production of a negative electrode] The metal lithium rolled plate was pierced with a diameter of 20mm in the shape of a disk, and the negative electrode was produced.

[0015] [Manufacture of nonaqueous electrolyte] To the solvent which shows composition in Table 1 - 6, a trifluoromethane sulfonic-acid lithium (LiCF<sub>3</sub>SO<sub>3</sub>) or one mol (LiPF<sub>6</sub>) / of hexafluoro phosphoric-acid lithiums was melted i., and nonaqueous electrolyte was prepared to it.

[0016]

[Table 1]

溶媒組成比 (体積比)	溶質	自己放電率 (%)
EC:DME = 50:50 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	14
EC:DME:トリメチル = 47.5:47.5:5 (本発明電池 X)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:n-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	3
EC:DME:γ-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	3
EC:DME:トリメチルフォスフィン = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:1-ブチル-2-メチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:γ-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:γ-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:3-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:γ-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:γ-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:γ-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:γ-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:N,N-ジメチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:N,N-ジメチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:トリメチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:N,N-ジメチル-2-エチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	3
EC:DME:N,N'-ジメチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	3
EC:DME:γ-ブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	3
EC:DME:3,5-ジブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	3
EC:DME:3-ブチル-2-メチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	3
EC:DME:1,2,3-トリブチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:N-メチル = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4

[0017]

[Table 2]

溶媒組成比 (体積比)	溶質	自己放電率 (%)
BC:DME:ジメチルスルホキシド =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:エチルメチルケトン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:2-メチルテトラヒドロフラン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:1-ブタンチオール =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:ペンタチオール =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:ジメチルホルムエーテル =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:ジエチルホルムエーテル =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:ジメチルグリコライト =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	4
BC:DME:ジエチルグリコライト =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:7-タリエンソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	4
BC:DME:3-メチルチオソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:1,4-チオソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:7,8-チオソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:1,4-チオソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:チオモルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	4
BC:DME:トリソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:1,3-ジメチル-2-メチルトリソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	3
BC:DME:ジメチルチオソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:ジメチルソルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	3
BC:DME:チオエチルチオモルボン =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	5
BC:DME:ジメチルスルホキシド =47.5:47.5:5	(本発明電池) LiClF, SO <sub>2</sub>	4

[0018]

[Table 3]

溶媒組成比 (体積比)		溶質	自己放電率 (%)
EC	= 100	LiCF <sub>3</sub> SO <sub>3</sub> LiCF <sub>3</sub> SO <sub>3</sub>	1.8 5
EC:トリエチレンソル	= 95:5		

[0019]

[Table 4]

溶媒組成比 (体積比)	溶質	自己放電率 (%)
EC:DME = 50:50 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	19
EC:DME = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
PC:DME = 50:50 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	16
PC:DME = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
BC:DME = 50:50 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	14
BC:DME = 47.5:47.5:5 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME = 50:50 (比較電池)	LiPF <sub>6</sub>	21
EC:DME = 47.5:47.5:5 (本発明電池)	LiPF <sub>6</sub>	5
PC:DME = 50:50 (比較電池)	LiPF <sub>6</sub>	18
PC:DME = 47.5:47.5:5 (本発明電池)	LiPF <sub>6</sub>	5
BC:DME = 50:50 (比較電池)	LiPF <sub>6</sub>	16
BC:DME = 47.5:47.5:5 (本発明電池)	LiPF <sub>6</sub>	4

[0020]

[Table 5]

溶媒組成比 (体積比)	溶質	自己放電率 (%)
EC:PC:DME = 1 : 1 : 1 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 4
EC:PC:DME : トリエチルアミン = 32:32:32:4 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:EC:DME = 1 : 1 : 1 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 3
EC:EC:DME : トリエチルアミン = 32:32:32:4 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
PC:EC:DME = 1 : 1 : 1 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 3
PC:EC:DME : トリエチルアミン = 32:32:32:4 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4

[0021]

[Table 6]

添加劑組成比 (體積比)	溶質	自己放電率 (%)
EC:DME:トリエチルミン = 49.95:49.95:0.1 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 3
EC:DME:トリエチルミン = 49.75:49.75:0.5 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 2
EC:DME:トリエチルミン = 49.5:49.5:1 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:トリエチルミン = 45:45:10 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:トリエチルミン = 40:40:20 (本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:トリエチルミン = 35:35:30 (比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	1 8

[0022] [Assembly of a cell] The nonaqueous electrolyte cell of various flat types was assembled using the above positive electrode, negative electrode, and nonaqueous electrolyte (cell size : 2.5mm in the diameter

of 20.0mm, thickness). In addition, as separator, the fine porous membrane made from polypropylene was used, and previous nonaqueous electrolyte was infiltrated into this.

[0023] [Rate of self-discharge of each cell] The service capacity C2 in 25 degreeC after saving for two months by the service capacity C1 in 25 degreeC immediately after the cell assembly of each cell and 80 degreeC was calculated, and the rate of self-discharge after preservation of each cell was computed by the lower formula. Altogether, by constant resistance of 1kohm, service capacity C1 and C2 discharges, and is calculated. A result is shown in previous Table 1 - 6. in addition, front Naka and EC — ethylene carbonate — PC — propylene carbonate — BC — butylene carbonate — moreover, DME expresses 1 and 2-dimethoxyethane, respectively

[0024]

Rate (%) of self-discharge  $= (1 - C2/C1) \times 100$ . [0025] As shown in Table 1 - 5, this invention cell which used the nonaqueous electrolyte (each additive content is 5 volume %) containing a specific additive has a low rate of self-discharge compared with the comparison cell by which the solvent and solute which do not contain an additive used the same nonaqueous electrolyte. This shows that the nonaqueous electrolyte cell which was excellent in the preservation property by making nonaqueous electrolyte contain a specific additive is obtained.

[0026] Moreover, since the rate of self-discharge is low compared with this invention cell Y in Table 3, when this invention cell X in Table 1 uses the mixed solvent of a high-rate-discharge solvent and 1 and 2-dimethoxyethane show that the nonaqueous electrolyte cell which was further excellent in the preservation property is obtained.

[0027] Furthermore, if additive content separates from this range to a thing with the very as low rate of self-discharge as 5% when additive content is made into one to 20 volume % as shown in Table 6, the rate of self-discharge will become high. This shows that it is necessary to regulate the additive content of nonaqueous electrolyte in the range of 1 - 20 volume %.

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(71) 出願人 000001889

三洋電機株式会社

大阪府守口市京阪本通2丁目5番5号

(72) 発明者 神野 丸男

大阪府守口市京阪本通2丁目5番5号 三  
洋電機株式会社内

(72) 発明者 上原 真弓

大阪府守口市京阪本通2丁目5番5号 三  
洋電機株式会社内

(72) 発明者 桜井 敦志

大阪府守口市京阪本通2丁目5番5号 三  
洋電機株式会社内

(74) 代理人 弁理士 松尾 智弘

最終頁に続く

(54) 【発明の名称】 非水電解液電池

(57) 【要約】

【構成】 エチレンカーボネート、プロピレンカーボネート及びブチレンカーボネートよりなる群から選ばれた少なくとも一種の高誘電率溶媒を含有する溶媒にトリフルオロメタンスルホン酸リチウム又はヘキサフルオロリン酸リチウムを溶かしてなる非水電解液に、特定の添加剤が1～20体積%添加されている。

【効果】 添加剤がリチウムなどと反応して負極の表面に被膜を形成し、この被膜が負極と非水電解液の反応を起こりにくくするので、長期間保存した場合でも自己放電が起こりにくい。このため、本発明電池は、保存特性に優れる。

(2)

## 【特許請求の範囲】

【請求項1】正極と、リチウムを活物質とする負極と、エチレンカーボネート、プロピレンカーボネート及びブチレンカーボネートよりなる群から選ばれた少なくとも一種の高誘電率溶媒を含有する溶媒にトリフルオロメタンスルホン酸リチウム又はヘキサフルオロリン酸リチウムを溶かしてなる非水電解液と、セパレータとを備える非水電解液電池であって、前記非水電解液が、トリエチルアミン、*n*-ブチルアミン、アニリン、トリメチルヒドロキシルアミン、1-ジメチルアミノ-2-メトキシエタン、アセトニトリル、アクリロニトリル、3-メトキシプロピオニトリル、ベンゾニトリル、ニトロメタン、ニトロエタン、N、N-ジメチルアセトアミド、N、N-ジメチルホルムアミド、ホルムアミド、N-メチル-2-ピロリドン、N、N'-ジメチルイミダゾリジノン、イソキサゾール、3, 5-ジメチルイソキサゾール、3-メチル-2-オキサゾリドン、1, 2, 3-オキサジアゾール、N-メチルモルホリン、ジメチルスルフィド、エチルメチルスルフィド、2-メチルチオフェン、1-ブタンチオール、ベンゼンチオール、ジメチルサルフェート、ジエチルサルフェート、ジメチルサルファイト、ジエチルサルファイト、ブタジエンスルホン、3-メチルスルホレン、1, 4-チオキサン、フェノキサチン、1, 4-チアジン、チオモルホリン、ピリジン、1, 3-ジメチル-2-イミダゾリジノン、ジメチルスルホキシド、ジメチルスルホン、メチルエチルスルホネート及びジメチルスルフィナイトよりなる群から選ばれた少なくとも1種の添加剤を1~20体積%含有することを特徴とする非水電解液電池。

【請求項2】前記非水電解液がさらに1, 2-ジメトキシエタンを含有する請求項1記載の非水電解液電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、非水電解液電池に係わり、詳しくは非水電解液電池の保存特性を改善することを目的とした、非水電解液の改良に関する。

## 【0002】

【従来の技術及び発明が解決しようとする課題】近年、リチウムを活物質とする負極を備える非水電解液電池が、正極の活物質を適宜選定することにより高容量化が可能なることから注目されている。

【0003】ところで、リチウムを活物質とする負極としては、金属リチウム、リチウム合金、炭素材料などが提案されている。

【0004】しかしながら、これらの負極材料は一般に保存中に非水電解液と反応し易く、このためリチウムを負極の活物質とする非水電解液電池には、長期間保存すると自己放電により放電容量が著しく減少するという問題がある。

【0005】本発明は、この問題を解決するべくなされ

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たものであって、その目的とするところは、負極と非水電解液との反応に起因する自己放電を抑制することにより、優れた保存特性を有する非水電解液電池を提供するにある。

## 【0006】

【課題を解決するための手段】上記目的を達成するための本発明に係る非水電解液電池（本発明電池）は、正極と、リチウムを活物質とする負極と、エチレンカーボネート、プロピレンカーボネート及びブチレンカーボネートよりなる群から選ばれた少なくとも一種の高誘電率溶媒にトリフルオロメタンスルホン酸リチウム又はヘキサフルオロリン酸リチウムを溶かしてなる非水電解液と、セパレータとを備える非水電解液電池であって、前記非水電解液が、トリエチルアミン、*n*-ブチルアミン、アニリン、トリメチルヒドロキシルアミン、1-ジメチルアミノ-2-メトキシエタン、アセトニトリル、アクリロニトリル、3-メトキシプロピオニトリル、ベンゾニトリル、ニトロメタン、ニトロエタン、N、N-ジメチルアセトアミド、N、N-ジメチルホルムアミド、ホルムアミド、N-メチル-2-ピロリドン、N、N'-ジメチルイミダゾリジノン、イソキサゾール、3, 5-ジメチルイソキサゾール、3-メチル-2-オキサゾリドン、1, 2, 3-オキサジアゾール、N-メチルモルホリン、ジメチルスルフィド、エチルメチルスルフィド、2-メチルチオフェン、1-ブタンチオール、ベンゼンチオール、ジメチルサルフェート、ジエチルサルフェート、ジメチルサルファイト、ジエチルサルファイト、ブタジエンスルホン、3-メチルスルホレン、1, 4-チオキサン、フェノキサチン、1, 4-チアジン、チオモルホリン、ピリジン、1, 3-ジメチル-2-イミダゾリジノン、ジメチルスルホキシド、ジメチルスルホン、メチルエチルスルホネート及びジメチルスルフィナイトよりなる群から選ばれた少なくとも1種の添加剤を1~20体積%含有する。

【0007】本発明電池の非水電解液は特定の添加剤を1~20体積%含有する。添加剤含有率がこの範囲を外れると、保存特性が向上しにくくなる。

【0008】非水電解液の溶媒として、上記高誘電率溶媒に1, 2-ジメトキシエタンを加えた混合溶媒を使用すれば、保存特性をさらに改善することができる。その場合の高誘電率溶媒と1, 2-ジメトキシエタンとの好適な含有比は、体積比で3:7~7:3の範囲である。

【0009】リチウムを活物質とする負極の具体例としては、リチウム合金（リチウム・アルミニウム合金、リチウム・鉛合金、リチウム・錫合金など）、金属酸化物（ $\text{LiNb}_2\text{O}_5$  など）又は炭素材料（黒鉛、コークス、有機物焼成体など）を負極材料に使用したものが挙げられる。

【0010】本発明は、特定の負極と特定の非水電解液とを備える非水電解液電池の保存特性を改善するべく、



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非水電解液として特定の添加剤を所定量含有するものを使用した点にその特徴が有る。したがって、正極、セパレータなどの電池を構成する他の部材については、非水電解液電池用として従来提案乃至実用されている種々のものを使用することができる。また、本発明は、一次電池及び二次電池の両方に適用可能なものである。

## 【0011】

【作用】非水電解液に含有させた特定の添加剤と、非水電解液中の溶媒・溶質及び負極中のリチウムとが反応して、負極表面に被膜が形成される。この被膜により、負極と非水電解液との反応が起こりにくくなるので、自己放電が抑制される。その結果、長期間保存した場合でも放電容量が減少しにくくなる（保存特性の向上）。なお、被膜は電子電導性が良好であるので、負極に被膜が形成されることにより負極における電極反応が阻害されることはない。

## 【0012】

【実施例】以下、本発明を実施例に基づいてさらに詳細に説明するが、本発明は下記実施例に何ら限定されるものではなく、その要旨を変更しない範囲において適宜変 \* 20

\* 更して実施することが可能なものである。

【0013】〔正極の作製〕活物質としての二酸化マンガ（ $375^{\circ}\text{C}$ で熱処理した二酸化マンガ）と、導電剤としてのアセチレンブラックと、結着剤としてのポリフッ化ビニリデンとを、重量比80:10:10で混合して正極合剤を調製し、この正極合剤をN-メチル-2-ピロリドンに分散させてスラリーを調製し、このスラリーをアルミニウム箔上に塗布し、圧延し、直径20mmの円盤状に打ち抜いた後、 $150^{\circ}\text{C}$ で2時間熱処理して、正極を作製した。

【0014】〔負極の作製〕金属リチウム圧延板を直径20mmの円盤状に打ち抜いて、負極を作製した。

【0015】〔非水電解液の調製〕表1～表6に組成を示す溶媒に、トリフルオロメタンスルホン酸リチウム（ $\text{LiCF}_3\text{SO}_3$ ）又はヘキサフルオロリン酸リチウム（ $\text{LiPF}_6$ ）を1モル/リットル溶かして非水電解液を調製した。

## 【0016】

【表1】

溶媒組成比（体積比）		溶質	自己放電率（%）
EC:DME	= 50:50	(比較電池)	
EC:DME:トリフルオロメタン	= 47.5:47.5:5	(本発明電池X)	14
EC:DME:n-ブチルアミン	= 47.5:47.5:5	(本発明電池)	5
EC:DME:7-47	= 47.5:47.5:5	(本発明電池)	8
EC:DME:トリフルオロメタン	= 47.5:47.5:5	(本発明電池)	3
EC:DME:1-ブチルピペリジン-2-チオール	= 47.5:47.5:5	(本発明電池)	5
EC:DME:7-チオニトリル	= 47.5:47.5:5	(本発明電池)	4
EC:DME:7-チオニトリル	= 47.5:47.5:5	(本発明電池)	4
EC:DME:3-チオニトリル	= 47.5:47.5:5	(本発明電池)	5
EC:DME:ペンチニトリル	= 47.5:47.5:5	(本発明電池)	5
EC:DME:ニトロメタン	= 47.5:47.5:5	(本発明電池)	4
EC:DME:ニトロメタン	= 47.5:47.5:5	(本発明電池)	5
EC:DME:N,N-ジメチルアセチル	= 47.5:47.5:5	(本発明電池)	4
EC:DME:N,N-ジメチルアセチル	= 47.5:47.5:5	(本発明電池)	5
EC:DME:4-メチル	= 47.5:47.5:5	(本発明電池)	4
EC:DME:N-メチル-2-ピロリドン	= 47.5:47.5:5	(本発明電池)	5
EC:DME:N,N'-ジメチルイミダゾリジン	= 47.5:47.5:5	(本発明電池)	3
EC:DME:4-メチル	= 47.5:47.5:5	(本発明電池)	3
EC:DME:3,5-ジメチルイソキサール	= 47.5:47.5:5	(本発明電池)	3
EC:DME:3-メチル-2-チオチオラド	= 47.5:47.5:5	(本発明電池)	3
EC:DME:1,2,3-チオチオラド	= 47.5:47.5:5	(本発明電池)	3
EC:DME:N-メチルピペリジン	= 47.5:47.5:5	(本発明電池)	4
		$\text{LiCF}_3\text{SO}_3$	4

## 【0017】

【表2】

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溶媒組成比 (体積比)			溶質	自己放電率 (%)
EC:DME:ジメチルスルホキシド	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:エチルジメチルスルホキシド	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:2-メチルテトラヒドロフラン	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:1-ブタンジオール	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:ペンタジオール	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:ジメチルホルムアミド	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:ジエチルホルムアミド	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:ジメチルアセトアミド	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:γ-ブチロラクトン	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:3-メチルブタノール	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:1,4-ジオキサン	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:7,7,8,8-テトラフルオロ-3,6-ジオキサン	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:1,4-ジオキサン	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:チオトルエン	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:エリツ	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME:1,3-ジメチル-2-イミダゾリノン	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:ジメチルホスフィン	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:ジメチルアセトアミド	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:メチルエチルアセトアミド	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	3
EC:DME:ジメチルアセトアミド	=47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4

【0018】

\* \* 【表3】

溶媒組成比 (体積比)			溶質	自己放電率 (%)
EC	= 100	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	18
EC:トリエチルアミン	= 95:5	(本発明電池 Y)	LiCF <sub>3</sub> SO <sub>3</sub>	5

【0019】

※ ※ 【表4】

溶媒組成比 (体積比)			溶質	自己放電率 (%)
EC:DME	= 50:50	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	10
EC:DME:トリエチルアミン	= 47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
PC:DME	= 50:50	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	16
PC:DME:トリエチルアミン	= 47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME	= 50:50	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	14
EC:DME:トリエチルアミン	= 47.5:47.5:5	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:DME	= 50:50	(比較電池)	LiPF <sub>6</sub>	21
EC:DME:トリエチルアミン	= 47.5:47.5:5	(本発明電池)	LiPF <sub>6</sub>	5
PC:DME	= 50:50	(比較電池)	LiPF <sub>6</sub>	18
PC:DME:トリエチルアミン	= 47.5:47.5:5	(本発明電池)	LiPF <sub>6</sub>	5
EC:DME	= 50:50	(比較電池)	LiPF <sub>6</sub>	16
EC:DME:トリエチルアミン	= 47.5:47.5:5	(本発明電池)	LiPF <sub>6</sub>	4

【0020】

★ ★ 【表5】

溶媒組成比 (体積比)			溶質	自己放電率 (%)
EC:PC:DME	= 1:1:1	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	14
EC:PC:DME:トリエチルアミン	= 32:32:32:4	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
EC:EC:DME	= 1:1:1	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	13
EC:EC:DME:トリエチルアミン	= 32:32:32:4	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4
PC:EC:DME	= 1:1:1	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	13
PC:EC:DME:トリエチルアミン	= 32:32:32:4	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	4

【0021】

☆ ☆ 【表6】

添加剤組成比 (体積比)			溶質	自己放電率 (%)
EC:DME:トリエチルアミン	= 49.95:49.95:0.1	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	13
EC:DME:トリエチルアミン	= 49.75:49.75:0.5	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	12
EC:DME:トリエチルアミン	= 49.5:49.5:1	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:トリエチルアミン	= 45:45:10	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:トリエチルアミン	= 40:40:20	(本発明電池)	LiCF <sub>3</sub> SO <sub>3</sub>	5
EC:DME:トリエチルアミン	= 35:35:30	(比較電池)	LiCF <sub>3</sub> SO <sub>3</sub>	18

【0022】〔電池の組立〕以上の正極、負極及び非水電解液を用いて種々の扁平型の非水電解液電池を組み立てた（電池寸法：直径20.0mm、厚さ2.5mm

m）。なお、セパレータとしては、ポリプロピレン製の微多孔膜を使用し、これに先の非水電解液を含浸させた。

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【0023】〔各電池の自己放電率〕各電池の電池組立直後の25°Cでの放電容量C1及び80°Cで二箇月保存した後の25°Cでの放電容量C2を求めて、各電池の保存後の自己放電率を、下式により算出した。放電容量C1、C2は、全て1kΩの定抵抗で放電して求めたものである。結果を先の表1～表6に示す。なお、表中、ECはエチレンカーボネートを、PCはプロピレンカーボネートを、BCは、ブチレンカーボネートを、またDMEは1, 2-ジメトキシエタンを、それぞれ表す。

【0024】

自己放電率(%) =  $(1 - C2/C1) \times 100$

【0025】表1～表5に示すように、特定の添加剤を含有する非水電解液（添加剤含有率はいずれも5体積%）を使用した本発明電池は、添加剤を含有しない溶媒及び溶質が同じ非水電解液を使用した比較電池に比べて、自己放電率が低い。このことから、非水電解液に特定の添加剤を含有させることにより、保存特性に優れた

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非水電解液電池が得られることが分かる。

【0026】また、表1中の本発明電池Xが、表3中の本発明電池Yに比べて自己放電率が低いことから、高率放電溶媒と1, 2-ジメトキシエタンとの混合溶媒を使用することにより、より一層保存特性に優れた非水電解液電池が得られることが分かる。

【0027】さらに、表6に示すように、添加剤含有率を1～20体積%とした場合は、自己放電率が5%と極めて低いのに対して、添加剤含有率がこの範囲を外れると自己放電率が高くなる。このことから、非水電解液の添加剤含有率を1～20体積%の範囲に規制する必要があることが分かる。

【0028】

【発明の効果】添加剤がリチウムなどと反応して負極の表面に被膜を形成し、この被膜が負極と非水電解液の反応を起りにくくするので、長期間保存した場合でも自己放電が起りにくい。このため、本発明電池は、保存特性に優れる。

フロントページの続き

(72)発明者 西尾 晃治  
大阪府守口市京阪本通2丁目5番5号 三  
洋電機株式会社内

(72)発明者 斎藤 俊彦  
大阪府守口市京阪本通2丁目5番5号 三  
洋電機株式会社内